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# Silica grain catalysis of methanol formation

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**ABSTRACT**

The specific catalytic effect of a silica grain on the formation of methanol *via* the sequential addition of H atoms to CO adsorbed on the surface is investigated. A negatively charged defect on a siliceous edingtonite surface is found to reduce the gas phase barriers for the $H + CO_{ads}$ and $H + H_2C{=}O_{ads}$ reactions by 770 and 399 K, respectively, when compared to the same reactions in the gas phase. The catalytic effect of negatively charged surface sites could also be applicable to the hydrogenation of other adsorbed unsaturated species. However, the activation energies on the surface defect are still too large (1150 and 2230 K) for $CH_3OH$ to form efficiently at 10–20 K in the interstellar medium via a classical mechanism. It is therefore suggested that quantum mechanical tunnelling through the activation barrier is required for these hydrogen addition reactions to proceed at such temperatures. The calculations show that because the adsorption energies of CO and $H_2C{=}O$ on the negatively charged defect are substantial, $CH_3OH$ may form efficiently during the warm-up period in star-forming regions.

**Key words:** astrochemistry — molecular processes — ISM: molecules.

## 1 INTRODUCTION

The formation of stars depends strongly on the presence of polar molecules that can act as coolants (Fraser, McCoustra & Williams 2002). Consequently, these stars are formed in molecular clouds, which are characterized by a high abundance and diversity of molecules, as well as dust grains that shield the molecules from the damaging effects of cosmic rays and ultraviolet radiation (Herbst 2005; van Dishoeck 2006). In cold molecular clouds, the low temperatures (10–20 K) mean that reactions with activation barriers of more than a few hundred K proceed very slowly. In massive star-forming regions, where temperatures can exceed 100 K, the observed gaseous species are thought to have desorbed after they have formed via extensive gas-grain chemistry (Millar & Hatchell 1998). The astrochemistry of these regions has been an active research area over the last decades, recently focusing on the role played by dust grains in catalysis (Williams & Herbst 2002; Williams et al. 2007). The comet dust captured by NASA's *Stardust* mission has shown unequivocally that some dust particles are made of crystalline silicate minerals such as forsterite.[1] There are also strong indications that a fraction of the dust grains consists of carbonaceous material (Millar & Williams 1993; Draine 2003), as reflected in the active astrochemistry research on the graphite surface (see Williams et al. 2007 for an extensive review).

One way in which dust grains could act as catalysts for astrochemical reactions is by reducing effective activation barriers. In this paper, we study, computationally, whether a siliceous surface can catalyze the formation of methanol. We use the (100) surface of edingtonite, a naturally occurring zeolite (Meier & Olson 1987), as our model grain surface. Methanol ($CH_3OH$) is one of the most-abundant molecular species observed in the interstellar medium (ISM) (Garrod et al. 2006), where it is usually found in water-rich interstellar ices frozen out on the surface of dust grains (Millar & Williams 1993; Pontoppidan et al. 2003). Since $CH_3OH$ has a much lower gas-phase abundance in molecular clouds, it is most likely formed on the surface of dust grains rather than freezing out after formation in the gas phase. The suggested route of formation is via the sequential addition of hydrogen atoms to CO (Tielens 1989; Tielens & Whittet 1997). However, experimental investigations of the formation of $CH_3OH$ from the bombardment of CO ices with hydrogen atoms have shown differing results (Hiraoka et al. 2002, 2005; Watanabe et al. 2004; Hiraoka, Mochizuki & Wada 2006; Hidaka, Kouchi & Watanabe 2007; Fuchs et al. 2007), although both formaldehyde ($H_2C{=}O$) and $CH_3OH$ have been observed as products at temperatures of 10–20 K. It has therefore been suggested that the formation of hydrogenated products could also be effected by photons (Hiraoka et al. 2002) or charged particles (Hiraoka et al. 2005) from the atom source. Indeed, Hudson & Moore (1999) have shown that $CH_3OH$ is formed efficiently upon irradiating a mixed $CO{:}H_2O$ ice with 0.8 MeV protons. The influence of water ice on the formation of $CH_3OH$ has been shown to be negligible in a previous computational study (Woon 2002). Here, we investigate computationally whether a negatively charged defect on a siliceous

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[1]http://www.nasa.gov/mission_pages/stardust/news/stardust-20060313.html

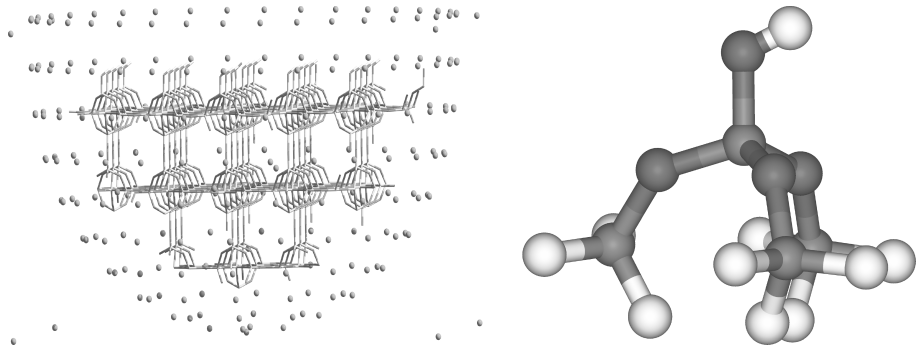

**Figure 1.** 25 Å radius hemispherical cluster cut from the (100) hydroxylated edingtonite surface with correcting charges (left-hand panel) and a picture of the atoms treated at the QM level for the silanol surface group (SiOH, right-hand panel). O: dark grey, Si: light grey, H: white.

surface (edingtonite) has a specific catalytic effect on the formation of $CH_3OH$ *via* the sequential addition of H to adsorbed CO. The catalytic effect of the hydroxylated edingtonite surface and a radicaloid defect on the same siliceous surface has also been investigated (Goumans et al., in preparation).

## 2 METHODOLOGY

We employ an embedded cluster approach in which a small cluster is treated with quantum mechanics (QM) and then embedded in a larger cluster, treated at the computationally cheaper molecular mechanics (MM) level (Fig. 1).

We use the modular CHEMSHELL code (Sherwood et al. 2003) with GAMESS-UK for the QM and DL_POLY for the MM calculations. The QM/MM boundaries ($Si_{QM}$–$O_{MM}$) are treated with a link-atom plus charge-shifting approach, as has been developed for zeolites (Sherwood et al. 2003). The model grain surface is the siliceous edingtonite (100) surface, which is a good computational model for an amorphous silica surface (Civalleri et al. 1999; Civalleri & Ugliengo 2000). A hemispherical cluster with a radius of 25 Å is cut from the fully optimized 2D surface (MM) and surrounded by charges to restore the Madelung potential. The QM cluster is treated with the B97-1 functional (Hamprecht et al. 1998), which has been shown to give good activation energies for hydrogen addition reactions (Goumans et al., in preparation; Andersson & Grüning 2004). We use a 6–31+G** (5D) basis for the adsorbates and the O and H atoms of the reactive surface site, and a 6–31G* (5D) basis for the remainder of the cluster. For the MM atoms, we use Hill & Sauer (1994) potentials , modified for use with DL_POLY (Goumans et al., in preparation). Unscaled zero-point energy corrections are included and energies are reported in Kelvin (1 K = 0.0083145 kJmol$^{-1}$) with three significant digits. Different QM cluster and active MM sizes have been considered to ensure that no artefacts arise from the QM/MM partitioning (Goumans et al., in preparation).

## 3 RESULTS

To benchmark our computational approach, we initially calculated the activation barriers for the gas-phase formation of $CH_3OH$. The following sequence of reactions is proposed for the formation of $CH_3OH$ from hydrogen atoms reacting with CO either in the gas phase or on a grain surface (Tielens & Whittet 1997; Woon 2002):

$$\mathrm{CO + H \rightarrow HCO + H \rightarrow H_2C{=}O + H \rightarrow CH_3O + H \rightarrow CH_3OH.}$$

**Table 1.** Calculated activation ($E^{\ddagger}$) and reaction energies ($E_{\mathrm{react}}$) in K for the consecutive hydrogenation of CO in the gas phase and adsorbed on a negatively charged surface defect via the Eley–Rideal mechanism.

| State | H + CO | | H + HCO | H + $H_2CO$ | | H + $CH_3O$ |
|---|---|---|---|---|---|---|
| | $E^{\ddagger}$ | $E_{\mathrm{react}}$ | $E_{\mathrm{react}}$ | $E^{\ddagger}$ | $E_{\mathrm{react}}$ | $E_{\mathrm{react}}$ |
| Gas phase | 1920 | −9510 | −42900 | 2630 | −12400 | −48700 |
| Adsorbed | 1150 | −15900 | −40400 | 2230 | −15200 | −54300 |

In this sequence, the first (H + CO) and third additions (H + $H_2C{=}O$) are activated in the gas phase, while the second and fourth additions are barrierless. We report the calculated activation and reaction energies in the gas phase and for the Eley–Rideal mechanism on the negatively charged surface defect in Table 1. Our calculated gas-phase barriers for the H + CO and H + $H_2C{=}O$ additions are 1920 and 2630 K, in good agreement with previous high-level calculations (Woon 1996, 2002; Andersson & Grüning 2004). The experimental barrier for H + CO is much lower (1000 K) than the high-level *ab initio* calculations, but this discrepancy could be due to other effects affecting the measured barrier, such as tunnelling (Woon 2002).

The perfect hydroxylated surface site (a silanol group, SiOH) was found not to lower the activation barriers of H + $CO_{ads}$ and H + $H_2C{=}O_{ads}$ with respect to their gas-phase values, while a radicaloid defect ($SiO^{\bullet}$) yielded higher barriers for the two activated reaction steps H + $HCO_{ads}$ and H + $H_2COH_{ads}$ (Goumans et al., in preparation). Therefore, in view of the negative equilibrium charge thought to be found on dust grains (Gail & Sedlmayer 1975), we consider here the effect of a negatively charged surface defect (silanolate, $SiO^-$) on the hydrogenation of adsorbed CO *via* the Eley–Rideal mechanism. The negatively charged defect is formed by the removal of a proton ($H^+$) from the silanol (SiOH) surface group.

CO is found to interact more strongly with an $SiO^-$ surface group than with an SiOH surface group, with adsorption energies of 2180 and 458 K, respectively. On adsorption at the $SiO^-$ site, the CO bond is stretched slightly from 1.139 Å (gas phase) to 1.148 Å. Concomitantly, the CO triple bond is weakened, resulting in a redshift of the CO vibration (−78 cm$^{-1}$). This weakening of the CO bond has a pronounced effect on the H + $CO_{ads}$ activation barrier, which is reduced by 770 K when compared to the gas phase, to only 1150 K on the defective siliceous surface (Table 1).

The subsequent addition of a hydrogen atom to the adsorbed HCO radical is barrierless (radical–radical addition) yielding adsorbed formaldehyde. Formaldehyde preferably adsorbs with one

of its hydrogen atoms pointing towards the $SiO^-$ defect. Like the triple bond in CO, the C=O bond of $H_2C{=}O$ is also weakened with respect to the gas phase ($\Delta r_{C=O} = 0.012$ Å, $\Delta h\nu = -51$ cm$^{-1}$), leading, again, to a reduction in the activation barrier for the third hydrogen addition with respect to the gas-phase barrier. The $H + H_2C{=}O$ barrier on the negatively charged surface defect is calculated to be 2230 K compared to 2630 K in the gas phase (Table 1). The resulting $SiO^-\cdots CH_3O$ intermediate can undergo a barrierless rearrangement with a hydrogen atom shifting from the carbon atom to the silanolate oxygen atom to yield $SiOH\cdots H_2CO^-$ (exothermic by 418 K). Both this complex and the initially formed $CH_3O_{ads}$ undergo barrierless addition of the fourth hydrogen atom to yield $CH_3OH_{ads}$.

Although there is a distinct catalytic effect of the negatively charged defect on the hydrogenation of CO to form $CH_3OH$, the two activation energies are still too high to give rise to significant classical reaction rates at 10–20 K. Hence, for these reactions to be effective at these temperatures on negatively charged siliceous dust grains there must be a strong tunnelling effect through the reaction barrier (Tielens and Hagen 1982). However, the reduction in the activation barrier by the negatively charged defect is likely to increase the reaction rate due to tunnelling as well. This catalytic effect could be ubiquitous for the hydrogenation of other unsaturated molecules such as acetaldehyde ($CH_3CH{=}O$), acetylene ($C_2H_2$), ethylene ($C_2H_4$) and hydrogen cyanide (HCN) where the double and triple bonds are also likely to be activated by the negative charge of the grain surface group.

## 4 ASTROPHYSICAL IMPLICATIONS

Because of the relatively large adsorption energies of CO and its hydrogenated derivatives on the $SiO^-$ group, the residence times of CO and $H_2C{=}O$ during turn-on of a star should be sufficient to give rise to formation of $CH_3OH$ on these defect sites. The ratio of the rate of reaction and the rate of desorption depends on the ratio of the respective pre-exponential factors and the differences in the activation energies for reaction and desorption (equation 1):

$$\frac{r_{\rm rxn}}{r_{\rm des}} = \frac{k_{\rm rxn}\theta_{\rm CO/H_2C=O}[{\rm H}]}{k_{\rm des}\theta_{\rm CO/H_2C=O}} = \frac{A_{\rm rxn}}{A_{\rm des}} e^{\left(-\Delta E^{\ddagger}_{\rm rxn}+\Delta E^{\ddagger}_{\rm des}\right)/T}[{\rm H}]. \quad (1)$$

In equation (1), $\theta_{\rm A}$ is the surface coverage of species A, [H] is the concentration of H atoms ($\theta_{\rm H}$ for a Langmuir–Hinshelwood mechanism, $n_{\rm H}$ for an Eley–Rideal mechanism), $r$ is the reaction rate, $k$ is the rate constant, $A$ is the pre-exponential factor, $T$ is the grain temperature in K and $\Delta E^{\ddagger}$ is the activation energy in K, while the subscripts 'rxn' and 'des' indicate reaction and desorption, respectively. Because adsorption of either CO or $H_2C{=}O$ on an $SiO^-$ site is barrierless, $\Delta E^{\ddagger}_{\rm des}$ is simply equal to the heat of adsorption of the species. At submonolayer coverage, desorption is of first order, with a typical pre-exponential factor ($A_{\rm des}$) of $\sim 10^{13}$ s$^{-1}$ (Kowalski 2002), while the typical pre-exponential factor of a bimolecular gas-phase reaction, or Eley–Rideal surface reaction, is $\sim 10^7$ m$^3$ mol$^{-1}$ s$^{-1}$ (Atkins & De Paula 2006). $A_{\rm rxn}$ could be calculated from the Eyring transition state theory (equation 2):

$$A_{\rm rxn} = e^2 \frac{k_b T}{h} e^{\frac{\Delta S^{\ddagger}_{\rm rxn}}{R}}, \quad (2)$$

where $k_{\rm b}$ is the Boltzmann constant, $h$ is the Planck constant, and $\Delta S^{\ddagger}_{\rm rxn}$ is the entropy of activation, which depends on the change in rotational, vibrational, and translational entropy. For a surface reaction, the change in rotational entropy is approximately zero, the change in vibrational entropy can be calculated from the vibrational modes of the reactant and the transition state, and the translational entropy of the incoming hydrogen atom is calculated from the translational partition function. This loss of translational entropy of the hydrogen atom is the main contributor to the activation entropy and cannot be obtained from static quantum chemical calculations, although it can be determined from thermodynamical integration of molecular dynamics simulations. However, if we estimate the hydrogen atom to be confined to a 'sample area' of 15 Å × 15 Å, the loss of translational entropy in the transition state would change the pre-exponential factor by a factor of $8 \times 10^{-2}$–$4 \times 10^{-2}$ from 10 to 20 K, which would give rise to an $A_{\rm rxn}$ for $H + CO_{ads}$ of $\sim$3–4 $\times 10^7$ m$^3$ mol$^{-1}$ s$^{-1}$. We note that the pre-exponential factor will be greatly enhanced at these temperatures when tunnelling is also taken into consideration. Since this estimate of the translational freedom of the hydrogen atom is rather arbitrary, and the calculated pre-exponential factor is strongly dependent on it, we use the textbook value of $A_{\rm rxn} \approx 10^7$ m$^3$ mol$^{-1}$ s$^{-1}$ in equation (1) and to calculate absolute reaction rates. This gives a value for $A_{\rm rxn}/A_{\rm des}$ of about $10^{-6}$ m$^3$ mol$^{-1}$. The activation energies and resulting rate proportionalities for reaction and desorption at 30 and 60 K, calculated with $A_{\rm rxn}/A_{\rm des} = 10^{-6}$ m$^3$ mol$^{-1}$, are summarized in Table 2.

**Table 2.** Hydrogenation and desorption activation energies in K and proportionality of the rate of reaction with H and rate of desorption at 30 and 60 K for CO and $H_2C{=}O$ adsorbed on an $SiO^-$ surface site.

| Species | $\Delta E^{\ddagger}_{\rm rxn}$ | $\Delta E^{\ddagger}_{\rm des}$ | $r_{\rm rxn}/r_{\rm des}$ (30 K) | $r_{\rm rxn}/r_{\rm des}$ (60 K) |
|---|---|---|---|---|
| CO | 1150 | 2180 | $9.24 \times 10^8 \times$ [H] | $3.04 \times 10^1 \times$ [H] |
| $H_2C{=}O$ | 2230 | 6040 | $1.59 \times 10^{49} \times$ [H] | $3.98 \times 10^{21} \times$ [H] |

Calculations using equation (1) show that CO is more likely to react with H via an Eley–Rideal mechanism than to desorb up to a temperature of 23 K with a hydrogen density $n_{\rm H}$ of $10^{-13}$ mol m$^{-3}$ ($\sim 10^4$ atoms cm$^{-3}$; Bakes 1997), whereas at these concentrations $H_2C{=}O$ is more likely to react with H than desorb up to 87 K. At these 'maximum' reaction temperatures, the activation energies calculated for these surface reactions give a classical rate of 2.1 $\times$ $10^{-35}$ mol m$^{-2}$ s$^{-1}$ ($1.3 \times 10^{-15}$ molecules cm$^{-2}$ s$^{-1}$) at 23 K for $H + CO_{ads}$ and $7.4 \times 10^{-25}$ mol m$^{-2}$ s$^{-1}$ ($4.5 \times 10^{-5}$ molecules cm$^{-2}$ s$^{-1}$) at 87 K for $H + H_2C{=}O_{ads}$, assuming a coverage of CO/$H_2C{=}O$ of approximately one per cent ($10^{-7}$ mol m$^{-2}$). Our calculations therefore indicate that on a negative defect on a siliceous surface, adsorption energies are increased while barriers are lowered, allowing for formation of $CH_3OH$ on a grain surface during the warm-up in star-forming regions, with $H_2C{=}O$ formation preceding $CH_3OH$ formation. While our calculated rates for the $H + CO_{ads}$ reaction and $H + H_2C{=}O_{ads}$ reaction are not very large, these rates will also be increased by quantum mechanical tunnelling through the reaction barrier as well as by local heating effects.

## 5 CONCLUSIONS

We have shown that a negatively charged defect on a siliceous surface ($SiO^-$) can catalyze the addition of hydrogen atoms to $CO_{ads}$ and $H_2C{=}O_{ads}$, reducing the activation barriers with respect to the gas phase by 770 and 399 K, respectively. The concomitant increase in adsorption energies of the unsaturated species on the negative surface defect increases residence times sufficiently to allow for effective formation of $H_2C{=}O$ up to 23 K and $CH_3OH$ up to 87 K during the warm-up period of a nearby forming star. Quantum mechanical tunnelling effects will further increase the reaction rates.

The catalytic effect stems from the destabilization of the unsaturated CO bond by the negative charge, resulting in bond stretching to a geometry more closely resembling that of the transition state. Presumably, by virtue of the same effect, negatively charged defects will similarly catalyze all radical additions to unsaturated bonds.

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## REFERENCES

Andersson S., Grüning M., 2004, J. Phys. Chem. A, 108, 7621
Atkins P., De Paula J., 2006, Physical Chemistry, 8th edn. Oxford University Press, Oxford
Bakes E. L. O., 1997, The Astrochemical Evolution of the Interstellar Medium. Twin Press, Vledder, the Netherlands
Civalleri B., Ugliengo P., 2000, J. Phys. Chem. B, 104, 9491
Civalleri B., Casassa S., Garrone E., Pisani C., Ugliengo P., 1999, J. Phys. Chem. B, 103, 2165
Draine B. T., 2003, ARA&A, 41, 241
Fraser H. J., McCoustra M. R. S., Williams D. A., 2002, Astron. Geophys., 43, 2.10
Fuchs G. W., Ioppolo S., Bisschop S. E., van Dishoeck E. F., Linnartz H., 2007, A&A, submitted
Gail H.-P., Sedlmayer E., 1975, A&A, 41, 359
Garrod R., Park I. H., Casselli P., Herbst E., 2006, Faraday Discuss., 133, 51
Hamprecht F. A., Cohen A. J., Tozer D. J., Handy N. C., 1998, J. Chem. Phys. 109, 6264
Herbst E., 2005, J. Phys. Chem. A, 109, 4017
Hidaka H., Kouchi A., Watanabe N., 2007, J. Chem. Phys., 126, 204707
Hill J.-R., Sauer J., 1994, J. Phys. Chem., 98, 1238
Hiraoka K., Sato. T., Sato S., Sogoshi N., Yokoyama T., Takashima H., Kitagawa S., 2002, ApJ, 577, 265
Hiraoka K. et al., 2005, ApJ, 620, 542
Hiraoka K., Mochizuki N., Wada A., 2006, in Kaiser R. I., Bernath P., Mebel A. M., Osamura Y., Petrie S., eds, AIP Conf. Proc. Vol. 855, Astrochemistry, From Laboratory Studies to Astronomical Observations. Am. Inst. Phys., New York, p. 86
Hudson R. L., Moore M. H., 1999, Icarus, 140, 451
Kowalski K. W., 2002, Surface Science. Wiley, Chichester
Meier W. M., Olson D. H., 1987, Atlas of Zeolite Structure Types. Butterworth, London
Millar T. J., Hatchell J., 1998, 2006, Faraday Discuss., 109, 15
Millar T. J., Williams, D. A., 1993, Dust and Chemistry in Astronomy. IOP Publishing, Bristol
Pontoppidan K. M., Dartois E., van Dishoeck E. F., Thi W. F., d'Hendecourt L., 2003, A&A, 404, L17
Sherwood P. et al., 2003, Theochem., 632, 1
Tielens A. G. G. M., 1989, in Allamandola L. J., Tielens A. G. G. M., eds, IAU Symp. Vol. 14, Interstellar Dust. Kluwer, Dordrecht, p. 239
Tielens A. G. G. M., Hagen W., 1982, A&A 114, 245
Tielens A. G. G. M., Whittet D. C. B., 1997, in van Dishoeck E. F., ed., Molecules in Astrophysics. Kluwer, Dordrecht, p. 45
van Dishoeck E. F., 2006, Proc. Natl. Acad. Sci. USA, 103, 12249
Watanabe N., Nagaoka A., Shiraki T., Kouchi A., 2004, ApJ, 616, 638
Williams D. A., Herbst E., 2002, Surf. Sci., 500, 823
Williams D. A., Brown W. A., Price S. D., Rawlings J. M. C., Viti S., 2007, Astron. Geophys., 48, 1.25
Woon D. E., 1996, J. Chem. Phys., 105, 9921
Woon D. E., 2002, ApJ, 569, 541

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